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Photon Echoes in Liquids on a 10-fs Time Scale

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Chemical reaction and optical dynamics in the liquid phase are strongly affected by specific solute-solvent interactions. The dynamical part of this coupling leads to energy fluctuations. It turns out that nonlinear optical spectroscopic techniques provide the key to map out the dynamics of the solute-solvent coupling underlying the optical lineshape. In case of solutions, pump-probe, transient hole burning, resonance Raman scattering and photon echo have been extensively used. In this contribution, we discuss the concept of photon echo in greater detail.

Femtosecond photon echo is well suited to probe solvation dynamics because it creates a time window through which this dynamical process can be monitored. For the last several years, a vast variety of different photon echo techniques that give the most direct access to the solvation dynamics process, have been developed. The "simplest" experiment is a special way of performing time-integrated photon echo, the so-called echo-peak shift. It was shown that the most remarkable feature of the echo peak-shift is that in many cases it reflects fairly well the solvation dynamics at most of the time scales. However, there are fundamental reasons for a complete failure of this experiment to represent the initial, most controversial part of solvation dynamics. A more advanced - and more difficult to accomplish - scheme employs time gating when the radiation emitted by the sample due to nonlinear interaction with the excitation pulses, is mixed with a gate pulse in a nonlinear optical crystal. In this way the echo intensity profile is mapped out in time, from which the system's dynamics at any time scale can be easily reconstructed.

Basically, both aforementioned techniques yield the information on the time scales of energy fluctuation around its mean position. However, they can not give any information on the time-dependant changes of the mean energy itself such as the dynamical Stokes shift. To do so, one needs to know the instantaneous frequency (or the phase) of the induced nonlinear polarization. This is accomplished by heterodyne detection of the photon echo. The echo signal is mixed on the quadratic detector with the local oscillator field which phase is locked to the echo. Moreover, the heterodyne detected photon echo has been shown to allow performing very special experiments such as suppressing interamolecular vibrational mode(s) that obscure the true solvation dynamics or exercising coherent control over nonlinear polarisation. It has been also shown that the spectral interferometry provides the same information as heterodyne-detected echo, being less experimentally involved.

The physics of the deduced correlation function is analysed in terms of under- and overdamped Brownian oscillators, representing intramolecular vibrations and solvent motions, respectively. The spectral density of the solvent motions, which dominate the solvation response, agrees well with the spectral density obtained from optical Kerr effect measurements in the case of acetonitrile, but in the case of ethylene glycol and other hydrogen-bonded solvents only the low-frequency parts overlap. This indicates that polarizability changes are not the only factor determining the effectiveness of the solute-solvent coupling. The fact that only a few Brownian oscillators are needed to simulate the complex optical dynamics of a dye molecule in solution validates the use of the multimode Brownian oscillator model for liquid state dynamics. The following step will be to project this parametrization onto a more microscopic model.

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Femtosecond vibrational spectroscopy as a tool for dynamical studies of site-specific excited-state solute-solvent interactions

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Solute-solvent interactions in liquids govern the ultrafast optical dynamics of vibronic excitations and play a key role in chemical reactions. Most of the experimental techniques applied so far on optical dephasing and solvation dynamics give no detailed information on local solute-solvent geometries and - thus - provide only limited insight into the microscopic mechanisms [1]. Here we demonstrate for the first time that vibrational spectroscopy can serve as a sensitive local probe. In particular, we show that the carbonyl functional group of coumarin dyes is affected by hydrogen-bonding with the solvent and analyze how this hydrogen bonding affects the optical dynamics. In the femtosecond measurements, coumarin 102 (C102) is excited to the S_1 state by a 100 fs pulse in the visible and the resulting change of the vibrational spectra is probed by 100 fs pulses tunable in the mid-infrared between 1500 and 1750 cm^{-1}.

For the case of nonpolar C_2Cl_4 as solvent, the transient change of absorbance (Fig. 1 b) shows a strong bleaching at the positions of the C=O stretching band around 1735 cm^{-1}, a frequency characteristic of a free carbonyl group, and of the ring mode at 1610 cm^{-1}. The transient spectra of excited molecules are derived from such data (symbols in Fig. 1 a) and demonstrate a decrease of the transition moments of these vibrations without significant spectral shifts. In the case of $CHCl_3$ as solvent, the ring mode also exhibits a transient bleach. However, a very different behavior of the C=O band is found. The C=O band in the electronic ground state in $CHCl_3$ is strongly down-shifted to 1700 cm^{-1}, indicating a strong hydrogen bond between solute and solvent. We observe a nearly complete bleaching of this ground-state C=O-mode and the appearance of a new band upshifted to 1740 cm^{-1} (see Fig. 2). The C=O stretch of C102 in the excited-state is located at about the same position as that in C_2Cl_4. These results indicate a total diminishing of the site-specific hydrogen-bonding interaction between the *C=O*-mode and $CHCl_3$ upon electronic excitation. In addition we show, for the first time, that by inspection of the time dependence of the IR-transmission changes of the C=O stretch in $CHCl_3$ after optical excitation the intermolecular hydrogen-bond between C102 and $CHCl_3$ is broken within 200 fs, with an additional dissociation of the solute-solvent complex within 3 ps.

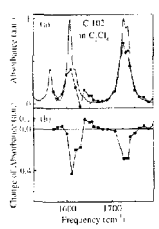

Figure 1: Ground- (solid) and excited-state (dots) IR-spectra (a) of C102 in C_2Cl_4. Time-resolved difference spectrum at 3 ps delay (b).

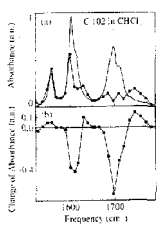

Figure 2: Ground- (solid) and excited-state (dots) IR-spectra (a) of C102 in $CHCl_3$. Time-resolved difference spectrum at 3 ps delay (b). The grey-shaded area shows the shifted C=O band.

[1] R. M. Stratt and M. Maroncelli, J. Phys. Chem. **100**, 12981 (1996).